Reversible Modification of the Si Environment in Template-free SAPO-34 Structure upon Hydration–Dehydration Cycles below *ca.* 400 K

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On hydration template-free SAPO-34 shows the opening of some Si–O–Al bonds as suggested by ^{29}Si MAS NMR and XRD results, the effect being reversible upon dehydration; the hydrated distorted structure is stable for months with no further modifications and the ordered material can be regenerated by removal of water at 423 K.

It has been shown that the structures of some aluminophosphates and AlPO$_4$-based materials are very sensitive to water at room temperature after template removal.[1–5] In the case of SAPO-34, an analogue of chabasite, it has been observed by ^{27}Al magic angle spinning (MAS) NMR that octahedral Al (Al^{VI}) formed during the hydration process recovers its tetrahedral coordination (Al^{IV}) by subsequent dehydration. This reversibility is observed during several hydration–dehydration cycles.[1] More recently X-ray diffraction (XRD)[6–8] has shown that the structure is strongly disturbed by water vapour below around 350–400 K[6,7] and that the decrease in crystallinity seen by XRD is reversible upon dehydration.[8] Preliminary ^{29}Si MAS NMR studies detected strong modifications of the spectra upon hydration.[6]

This paper demonstrates that the hydration–dehydration process involves significant reversible modifications of the Si environments. They are revealed by concomittant changes in the ^{29}Si MAS NMR spectra and XRD patterns.

SAPO-34 with formula (Si$_{0.09}$Al$_{0.50}$P$_{0.41}$)O$_2$ was synthesized as described previously[1,10] using tetraethylammonium hydroxide as template (TEAOH). The organic template was decomposed by heat treatment at 873 K in flowing air for 6 h and then in vacuum for 6 h. The complete removal of the template was checked by IR spectroscopy. It has been observed that incomplete removal of the template modifies the stability of the solid. The treated materials were kept anhydrous in sealed tubes for ^{29}Si MAS NMR and XRD studies. The samples were transferred either to the NMR rotor or to a waterproof XRD cell in a dry atmosphere. Several dehydration–hydration experiments were conducted on the template-free materials. They were reproducible and a typical set is reported here. The hydration step of the samples was allowed to proceed at room temp. in a 75% constant relative humidity. For further dehydration, the samples were transferred to a vacuum line and evacuated at 573 K. The ^{29}Si MAS NMR spectra were recorded in conditions used in previous SAPO studies[11] using

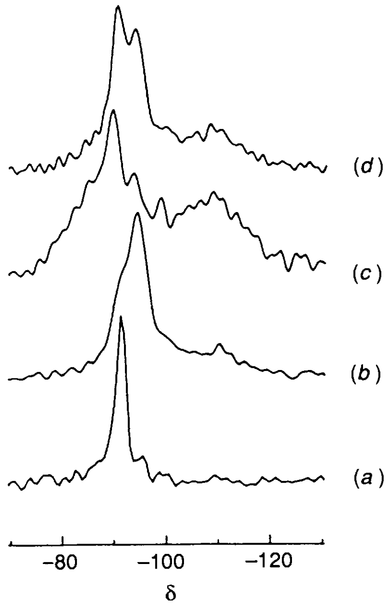

Fig. 1 ^{29}Si MAS NMR spectra of SAPO-34, (*a*) as synthesized, (*b*) after template removal in a dry atmosphere at 873 K, (*c*) sample (*b*) rehydrated at room temp. for 5 days, (*d*) evacuation of sample (*c*) for 10 h at 573 K

a MSL 400 Brüker spectrometer. The X-ray patterns were obtained with a Siemens D500 diffractometer.

Fig. 1 shows the ^{29}Si MAS NMR spectra of the samples. For the as-synthesized material a sharp peak of Si(4Al) is obtained at δ − 91.6 [spectrum (*a*)] with small peaks in the range δ − 95 to −110. Peaks in this range reveal the presence of some Si islands[11] in the as-made chabasite framework. After full removal of the template at 873 K the main peak, spectrum (*b*), is shifted to δ − 94.2 with a shoulder at around − 91. The peaks in the range δ − 95 to − 110 are slightly increased. Upon rehydration at room temp. for 5 days, the spectrum (*c*) is completely modified. A broad peak with a maximum at around δ −108.6 which may correspond to silica[12] is seen with other intense peaks at around δ − 93.6 and − 98.8. The most striking feature is the formation of intense peaks in the range δ − 75 to − 90. They are in the domain of Q^2 and Q^1 species.[12] The presence of hydroxy groups in these species was confirmed by the increase of the intensity of those peaks, the others being constant, using the cross polarization (CP) MAS technique. Further evacuation of the sample at 573 K for 10 h shows that the Q^2 and Q^1 species disappear and that the intensity of the peaks assigned to Si islands (δ −95 to − 110) is greatly decreased [spectrum (*d*)]. The results are identical for all the series of experiments performed whether the template removal is conducted in an oven at 873 K or in a vacuum line (air treatment then evacuation at the same temperature). Similar results are also observed if the rehydration (*c*) is conducted up to several weeks instead of a few hours or days.

Simultaneously with these changes, modifications are observed by XRD and the results are shown in Fig. 2. The as-synthesized sample gives a pattern similar to that which has already been published [spectrum (*a*)].[9] Template removal upon calcination and evacuation at 873 K induces some modification of relative intensities and *d*-spacing [spectrum (*b*)]. They are very similar to those very often observed with zeolites. No loss of crystallinity is noticed. However, rehydration for 15 h at room temp. decreases the intensity of the peaks by about 50% [spectrum (*c*)]. In addition a very broad peak at 2θ = 25° appears, suggesting the formation of a disordered phase. The X-ray pattern recovers its shape and intensity after evacuation at 573 K [spectrum (*d*)]. The 100% crystallinity is restored and the broad peak at 2θ = 25° disappears. Rehydration of up to several months gives similar good crystallinity after evacuation at 573 K. Even a lower evacuation temperature (423 K) is enough to regenerate the materials. It was previously shown[7] that the loss of intensity of X-ray lines upon rehydration occurs only if the temperature is lower than around 373 K.

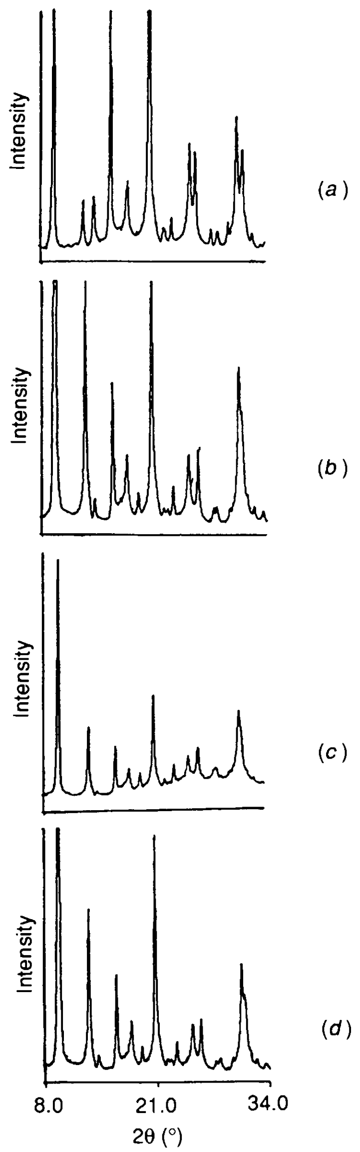

Fig. 2 XRD pattern of SAPO-34, (*a*) as synthesized, (*b*) after template removal in a dry atmosphere at 873 K, (*c*) sample (*b*) rehydrated at room temp. for 15 h, (*d*) evacuation of sample (*c*) for 10 h at 573 K

Table 1 Changes in the unit cell parameters and unit cell volume of various SAPO-34 samples

	As synthesised	After template removal at 873 K	After rehydration at room temp.	After dehydration at 573 K
a[a]	13.81	13.71	13.59	13.70
c[a]	14.80	15.00	14.91	14.93
V[b]	2443	2442	2385	2428

[a] In Å, accuracy ±0.03. [b] In Å^3, accuracy ±15.

Table 1 shows that the *a* parameter and the volume of the unit cell are similar for the organic-free sample just treated at 873 K or after it was hydrated and further dehydrated at 573 K. The rehydration at room temp. decreases all the values. These values are not affected by the rehydration time (from a few days up to 8 months).

In summary, ^{29}Si MAS NMR and XRD give complementary information on the disorders generated in SAPO-34 upon hydration at room temp. or below about 373 K. The information supports the proposal that Si–O–Al bonds are opened upon interaction with water to give Si–OH and Al–OH species. The broad δ -108.6 ^{29}Si MAS NMR peak [Fig. 1(*c*)] suggests that some new -Si–O–Si–O–Si- bonds would be formed, eventually from close Si–OH bonds. This would involve a strong distortion of the lattice. This modification would be responsible for the broad 2θ peak at 25° and the decrease of peaks of the chabasite structure in the X-ray pattern of the rehydrated materials (Fig. 2). Upon water evacuation the strains induced by the interaction of H_2O with some Si–O–Al bonds would be removed, resulting in reversibility of both the ^{29}Si MAS NMR and XRD results. This would be in line with the observed reversibility of the $Al^{VI} \rightarrow Al^{IV}$ NMR peaks upon dehydration.[1] The reversible interaction H_2O/SAPO-34 occurs within a few hours and is not modified over several months.

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